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# Open Source DSMC Chemistry Modelling for Hypersonic Flows

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## Abstract

An open source implementation of chemistry modelling for the direct simulation Monte Carlo (DSMC) method is presented. Following the recent work of Bird [1] an approach known as the quantum kinetic (Q-K) method has been adopted to describe chemical reactions in a 5-species air model using DSMC procedures based on microscopic gas information. The Q-K technique has been implemented within the framework of the *dsmcFoam* code, a derivative of the open source CFD code OpenFOAM. Results for vibrational relaxation, dissociation and exchange reaction rates for an adiabatic bath demonstrate the success of the Q-K model implementation in *dsmcFoam* when compared with analytical solutions for both inert and reacting conditions. A comparison is also made between the Q-K and total collision energy (TCE) chemistry approaches for a hypersonic flow benchmark case.

**Keywords:** *DSMC, open source, chemistry, non-equilibrium, rarefied gas, hypersonic, OpenFOAM*

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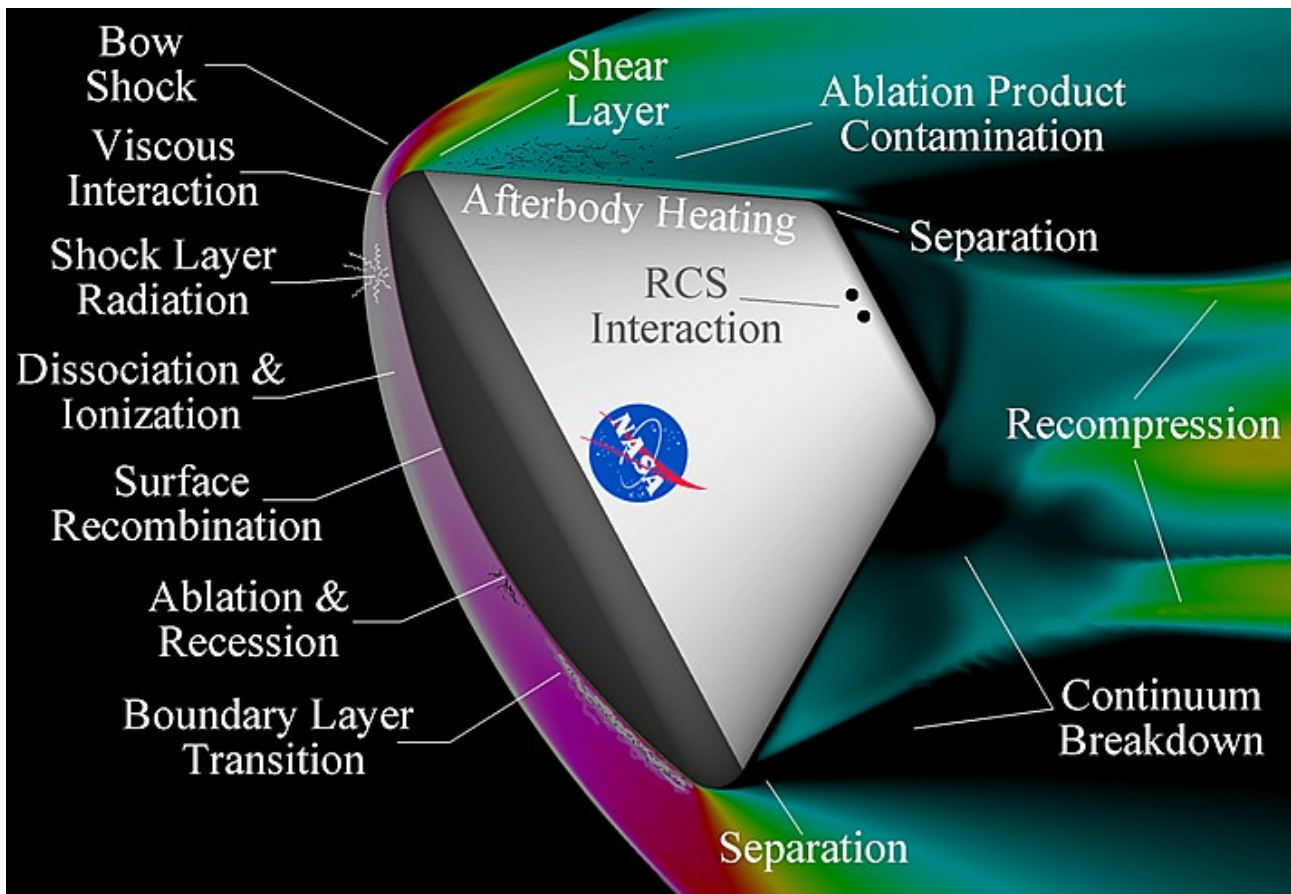
## 1. Introduction

Hypersonic vehicles, which typically operate in rarefied gas environments, are subject to extremes of velocity and altitude. So it is important that the aerodynamic and thermal loads on the vehicle are properly characterised if the feasibility of the vehicle design is to be accurately assessed. The vehicle may also encounter chemical reactions that can have a significant influence on aerodynamic performance and vehicle surface heat flux [2]. Numerical models that fail to incorporate such reacting flows miss an essential part of the flow physics surrounding the vehicle.

The planetary atmospheres through which hypersonic vehicles may pass consist of a number of chemical species, the relative proportion of which varies with altitude. Although the gas in the atmosphere is composed, at the microscopic level, of discrete atoms and molecules, a useful approximation arises if the atmosphere is treated as a continuum. The flow over a vehicle moving through the atmosphere can then be modelled by appealing to the fundamental principles of momentum interchange and mass and energy conservation. This continuum approach is at the root of conventional computational fluid dynamics (CFD) methods for the solution of the Navier-Stokes-Fourier (NSF) equations. Indeed, continuum CFD has been applied successfully in many simulations of gas flow around air- and spacecraft, and yields good agreement with measured data over a wide range of practically-relevant operational conditions [3].

However, continuum-based models have limitations in rarefied gas conditions. The extent of gas rarefaction is traditionally gauged by the Knudsen number,  $Kn$ , defined as the ratio of the mean free path of the gas molecules to a characteristic length scale of the vehicle. As the Knudsen number increases, the non-continuum, particulate-like behaviour of the gas becomes more important. Numerical models hoping to simulate

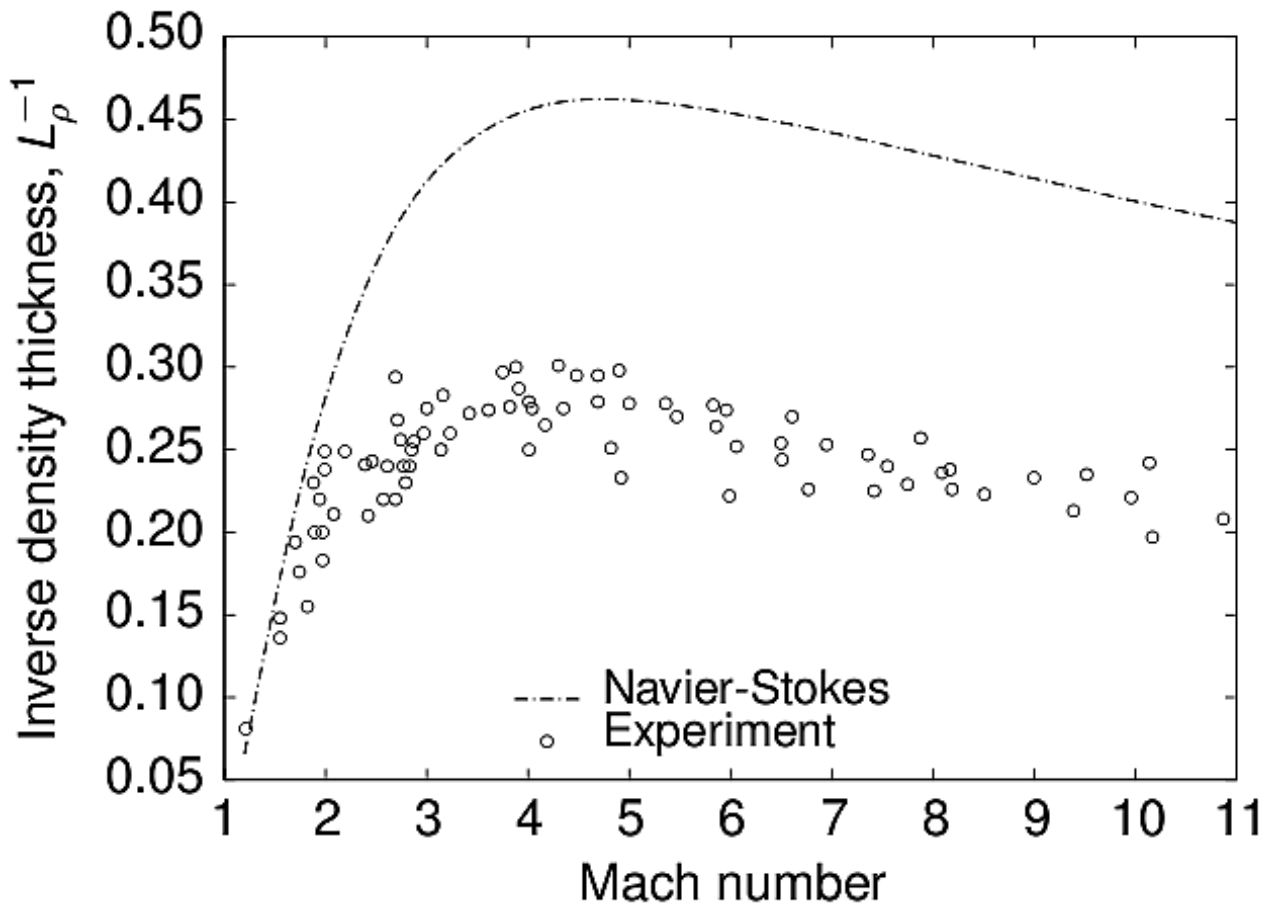
such rarefied conditions must be able capture the complex physics shown in Figure 1 for high-speed vehicle re-entry. The flow environment is characterised by a distinct bow-shock upstream of the body with a high temperature region immediately downstream of the shock. In this searingly hot region, chemical reactions may take place involving dissociation, exchange and ionization, while surface chemistry is also possible. In the wake of the craft there is a highly rarefied zone within which thermochemical non-equilibrium conditions may exist. The paucity of molecules in this zone may necessitate the region being described using a non-continuum, particle-based formulation.



**Figure 1** *Complex physics in planetary vehicle re-entry (image credit NASA).*

It may be possible to describe such complex flow conditions using the Boltzmann equation, which is appropriate for the entire range of Knudsen numbers likely to be encountered by hypersonic vehicles. However, the Boltzmann equation is extremely difficult to solve numerically due to its high dimensionality and the complexity of the collision term. Simplification of the collision term in the equation through the Bhatnagar–Gross–Krook (BGK) approximation [4] has given rise to a number of new numerical algorithms, such as the model Boltzmann equation (MBE) solver developed by Yang and Huang [5]; however these nascent techniques have yet to establish themselves as practical simulation tools, particularly for high-speed reacting flows.

The problem that the conventional Navier-Stokes-Fourier (NSF) equations have in capturing rarefaction is highlighted in Figure 2 [6]. The normal shock wave is a fundamental component of many high-speed aerodynamic flows, e.g. in the central



**Figure 2** *The inverse of the normalised density thickness of normal shock waves in argon gas up to Mach 11.*

part of the bow shock. Rarefaction causes the shock to be relatively thick (of the order of a few gas mean-free-paths - of the same order as the stand-off distance of the bow shock from the vehicle leading edge). This figure shows that the NSF equations consistently predict shocks in argon gas that are some 50% thinner than observed experimentally. That the fluid dynamic equations have such difficulty in predicting the behaviour in such a simple flow case, calls their appropriateness for more complex rarefied flow fields into question.

Non-continuum behaviour can be accommodated to some extent in conventional NSF

approaches to modelling the gas dynamics around aero-space vehicles, for instance by incorporating a finite slip velocity between the gas and any solid surfaces that are immersed within the flow. A computationally-efficient gas flow method, but one which has had only modest success to date, is to establish either a  $Kn$ -series or a Hermite polynomial approximation to the molecular velocity distribution function in the Boltzmann equation. To first order (i.e. for near-equilibrium flows) this approach yields the NSF set, but the solution method can be continued to second and higher orders to incorporate more and more of the salient characteristics of a rarefied flow. This family of so-called extended hydrodynamic equations has various different members, including the Burnett, Grad 13-moment, R13, R26 equations, and others. Generally, they all have great difficulty in achieving stable physical solutions of high-Mach-number flows. Their non-linearity also makes them difficult to solve numerically and, as they are higher-order in the gradients of flow properties, their solution requires additional boundary conditions that are not easy to define. For these reasons, extended hydrodynamics has not established a firm place in the armoury of tools a high-speed aerodynamicist can deploy.

### 1.1 *The Direct Simulation Monte Carlo (DSMC) method*

In highly rarefied environments ( $Kn > 0.1$ ) accommodation of the thermochemical non-equilibrium effects that occur in the flow away from surfaces remains a challenging problem. For this reason, analysis of gas flows in the non-continuum regime is most naturally conducted using specialised computational techniques that are derived from a statistical mechanical representation of the behaviour of the individual particles comprising the flow. The most successful of these techniques is undoubtedly the direct simulation Monte Carlo (DSMC) approach, originally proposed by Bird [7].

The DSMC technique instructs particles to move and collide using kinetic-theory considerations that can capture the non-continuum gas behaviour accurately. DSMC considers molecular collisions using stochastic rather than deterministic procedures over a time step which is a small fraction of the mean collision time, and each DSMC particle represents a large number of real gas molecules. The decoupling of particle ballistic motion and particle collisions improves the computational efficiency of DSMC greatly in comparison with other particle methods such as molecular dynamics (MD). The computational domain is divided into either a structured or unstructured grid of cells, with each cell of a dimension that is a small fraction of the local mean free path. The cells are then utilised to select particles for collisions on a probabilistic basis, and also are used for sampling the macroscopic flow properties. Intermolecular collisions are handled probabilistically using phenomenological models that are designed to reproduce real fluid behaviour when the flow is examined at the macroscopic level. The DSMC technique has been shown to provide a solution to the Boltzmann equation as the number of simulated particles tends toward infinity [8]. The DSMC approach is currently the dominant numerical method for rarefied gas flow applications.

## 1.2 *Thermochemistry effects*

For engineering purposes, the gas in the Earth's atmosphere may be assumed to be a binary mixture of oxygen ( $O_2$ ) and nitrogen ( $N_2$ ). In the DSMC methodology, particle clusters must be endowed with the correct properties to capture kinetic and rotational modes of energy storage. Vibrational excitation of the gas molecules as well as dissociation of both oxygen and nitrogen are likely to be important features of the flow around any hypersonic vehicle at the highest altitudes (80-120 km) and speeds, while even at lower speeds and altitudes vibrational excitation and limited dissociation of oxygen are still likely to be important [9]. Such real-gas effects need



to be properly accounted for. The DSMC technique normally models air as either a 5-species mixture using dissociation, recombination and exchange reactions, or as a mixture of 11-species including ionisation. In conventional CFD, reaction rates are calculated according to the Arrhenius law [9]. However, this relies on data sourced from equilibrium conditions, which may be inappropriate for rarefied hypersonic flows. In contrast, the DSMC method, with its particulate approach, is able to capture successfully the thermochemical non-equilibrium effects encountered in high speed rarefied gas environments [1, 2].

The goal of this work is to describe, verify and discuss the implementation of a state-of-the-art chemistry model, using the quantum-kinetic (Q-K) approach [1], in an open source, non-proprietary DSMC code for exploitation by the scientific community.

## **2. Chemistry modelling in *dsmcFoam***

The DSMC code used for this paper is called *dsmcFoam*. The code has been written within the framework of the open source C++ CFD toolbox OpenFOAM [10]. The main features of the *dsmcFoam* code include the capability to perform both steady and transient DSMC simulations for multi-species conditions, to model arbitrary 2D/3D geometries using unstructured polyhedral meshes, and unlimited parallel processing. The original version of *dsmcFoam* determines intermolecular collisions for polyatomic species using the variable hard sphere (VHS) model and applies the phenomenological Larsen-Borgnakke model to distribute post-collision energy between the translational and rotational modes [7]. A series of successful benchmark trials have been carried out to verify the *dsmcFoam* code for non-reacting flows [11].

## 2.1 Vibrational energy and the Q-K chemistry model

The vibrational energy mode plays a key role in chemical reactions using the Q-K model. This mode was excluded in previous versions of *dsmcFoam* [11] so this section describes the implementation and validation of the vibrational mode into the code. The vibrational modes of a gas are generally active when the system is sufficiently energised, e.g. under the high enthalpy conditions commonly found in hypersonic applications. The vibrational mode forms part of the total energy budget and limits the amount of post-collision energy available to the translational and rotational modes. In addition, it often introduces a new mode of non-equilibrium to a rarefied gas system as the number of collisions required for vibrational relaxation is significantly higher than that for translational or rotational equilibration.

For the implementation of the vibrational mode in *dsmcFoam* it is proposed that the vibrational energy can only assume discrete quantum values, as described by Haas *et al.* [12] and Bergman and Boyd [13]. We consider a serial application of the quantum Larsen-Borgnakke method using the harmonic oscillator model to redistribute vibrational energy before rotational and translational energy exchange are considered. It is desirable in DSMC to avoid the use of the macroscopic temperature whenever possible as colliding particles have no knowledge of the surrounding temperature. Here, we discuss a model for the redistribution of vibrational energy based on the collision energy (as opposed to the local macroscopic temperature of the gas). The first step is to define a “quantized collision temperature”,  $T_{coll}$ , based on the collision energy of a particle pair,  $p$  and  $q$ , [14]:

$$T_{coll} = \frac{i_{max} \theta_v}{\frac{7}{2} - \omega} , \quad (1)$$

where

$$i_{max} = \left\lfloor \frac{E_c}{k \theta_v} \right\rfloor, \quad (2)$$

and  $\lfloor \dots \rfloor$  denotes truncation,  $i_{max}$  is the maximum quantum level available to the molecule,  $\theta_v$  is the vibrational temperature,  $k$  is the Boltzmann constant,  $\omega$  is the temperature exponent of viscosity, and  $E_c$  is the sum of the relative translational energy of the collision pair and the pre-collision vibrational energy of the molecule under consideration, i.e.

$$E_c = \varepsilon_{tr,pq} + \varepsilon_{v,p}. \quad (3)$$

The vibrational collision number  $Z_v$  can then be calculated as [14]

$$Z_v = \left( \frac{\theta_d}{T_{coll}} \right)^\omega \left[ Z_{ref} \left( \frac{\theta_d}{T_{Zref}} \right)^{-\omega} \right] \left[ \left( \frac{\theta_d}{T_{coll}} \right)^{\frac{1}{3}-1} \right] / \left[ \left( \frac{\theta_d}{T_{Zref}} \right)^{\frac{1}{3}-1} \right], \quad (4)$$

where  $\theta_d$  is the characteristic dissociation temperature and  $Z_{ref}$  is the vibrational collision number at a reference temperature  $T_{Zref}$ , which is usually taken to be the characteristic vibrational temperature,  $\theta_v$ , such that [15],

$$Z_{ref} = \left( \frac{C_1}{T_{Zref}^\omega} \right) \exp \left( C_2 T_{Zref}^{-1/3} \right), \quad (5)$$

where  $C_1$  and  $C_2$  are constants which can be found in Appendix A of Ref [7], and  $T_{Zref}$  is set as  $\theta_v$ .

Once the vibrational collision number has been calculated, the particle is tested for vibrational energy exchange and is accepted if

$$\frac{1}{Z_v} > R_f, \quad (6)$$

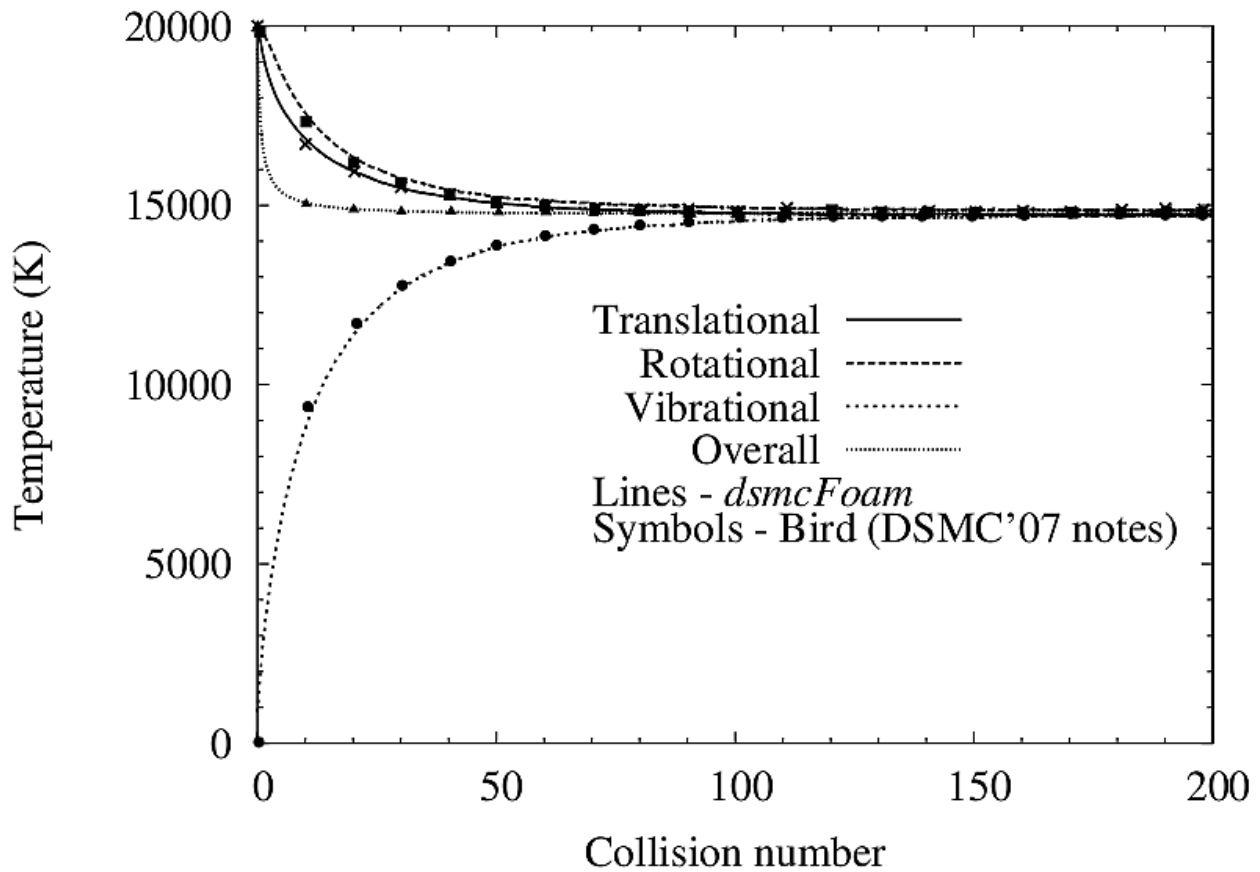
where  $R_f$  is a random number between 0 and 1. An integer post-collision vibrational quantum level  $i^*$  is chosen uniformly between 0 and the maximum possible level  $i_{max}^*$  and the acceptance-rejection method is used to select a value of  $i^*$  using a quantized version of the Larsen-Borgnakke probability ratio [13]:

$$\frac{P}{P_{max}} = \left( 1 - \frac{i^* k \theta_v}{E_c} \right). \quad (7)$$

The total energy of the pair is reduced accordingly, and particle  $p$  is then considered for relaxation into the rotational and translational modes using the standard Larsen-Borgnakke approach.

In order to verify the implementation of this vibrational energy exchange, a test case involving relaxation to equilibrium is considered. This test case involves an adiabatic box filled with nitrogen gas, in a similar manner to that considered by Bird [16]. The translational and rotational temperatures are initially 20,000 K and there is no energy in the vibrational mode. The reference vibrational collision number  $Z_{ref}$  is 19.8 at a reference temperature of 20,000 K. The *dsmcFoam* simulation is performed using the VHS collision model, with the following properties ascertained at  $T_{ref} = 273$  K:  $m = 46.5 \times 10^{-27}$  kg,  $\omega = 0.74$  and  $d_{ref} = 4.17 \times 10^{-10}$  m, where  $d_{ref}$  and  $m$  are the molecular diameter and mass, respectively.

The cell is filled with 1.2 million DSMC particles and, as the particles begin to collide, energy is transferred to the vibrational mode and equipartition is achieved at a temperature of around 14,720 K after a period of relaxation, as shown in Figure 3. The ‘collision number’ on the abscissa is calculated as the product of the instantaneous collision rate from the simulation and the physical time that has elapsed. The *dsmcFoam* results agree well with those of Bird’s DS2V code [16]. The rotational temperature follows the translational temperature closely and the vibrational temperature takes a longer time to arrive at equilibrium. The relaxation rates of all temperatures and the final equilibrium temperature are in good agreement with Bird’s results.



**Figure 3** *Vibrational relaxation of nitrogen gas.*

## 2.2 Quantum-kinetic chemical reactions

Until recently, chemically reacting gas flows in DSMC have relied upon input data derived at the macroscopic level and reaction rate coefficients that are derived from equilibrium theory. This method for treating chemical reactions was introduced by Bird in 1979 and is known as the “total collision energy” (TCE) model [17]. The TCE chemical reaction model is well established and is used in mature DSMC codes such as MONACO [18].

As an alternative approach, Bird has recently proposed a chemical reaction model that is founded on the quantum Larsen-Borgnakke method described in section 2.1. This model has only a limited dependence on macroscopic data as the vibrational collision number is a function of the collision temperature (microscopic level) and a reference temperature (macroscopic level). The method also does not require that the gas be in a state near thermodynamic equilibrium. This is termed the “quantum-kinetic” (Q-K) model, and it has been developed over the past five years [1, 2, 14, 19].

In this paper we consider dissociation and exchange reactions using the Q-K approach with the aim of creating a five-species (oxygen  $O_2$ , nitrogen  $N_2$ , nitric oxide  $NO$ , atomic oxygen  $O$ , and atomic nitrogen  $N$ ) air chemistry model for use in the open source *dsmcFoam* code.

## 2.3 Dissociation reactions

The condition for a dissociation reaction in the Q-K model is as follows: if the energy in a collision is high enough to allow a dissociation event, it will always occur. The reaction being considered is  $AB + C \rightarrow A + B + C$ , where  $AB$  is the molecule

considered for dissociation,  $C$  is the reactant partner (either a molecule or an atom) and  $A$  and  $B$  are the atomic products of the dissociation. Considering the serial application of the quantum Larsen-Borgnakke model, the collision energy  $E_c$  of a particle pair ( $AB + C$ ) is the sum of the relative translational energy and the pre-collision vibrational energy of the particle currently being considered, as described by Equation (3). The maximum vibrational level that can be selected  $i_{max}$  is given by Equation (2). If  $i_{max}$  is beyond the dissociation limit, i.e.

$$i_{max} > \frac{\theta_d}{\theta_v}, \quad (8)$$

then the molecule  $AB$  must be dissociated before any vibrational or rotational relaxation can be considered.

A distinct feature of the Q-K model is that although the DSMC implementation does not necessitate that the gas be in equilibrium, if it is assumed that it is, then analytical solutions for the reaction rates can be derived. For a VHS gas in equilibrium, the rate coefficient  $k_f(T)$  for the dissociation of a molecule  $AB$  with a molecule or atom  $C$  is

$$k_f(T) = R_{coll}^{AB,C} \gamma(i_{max})^{AB,C}, \quad (9)$$

where  $R_{coll}^{AB,C}$  is the collision rate between species  $AB$  and  $C$  divided by the number density product. For an equilibrium VHS gas, this is

$$R_{coll}^{AB,C} = \frac{2\pi^{1/2}}{\alpha} (r_{ref}^{AB} + r_{ref}^C)^2 \left( \frac{T}{T_{ref}} \right)^{1-\omega^{AB,C}} \left( \frac{2kT_{ref}}{m_r^{AB,C}} \right)^{1/2}, \quad (10)$$

where  $r_{ref}$ ,  $T_{ref}$  and  $\omega$  are the standard VHS properties of the relevant gas species,  $m_r$  is the reduced mass of the collision pair, and  $T$  is the macroscopic temperature of the gas. The symmetry factor  $\alpha$  is set to 2 if the molecules in the collision are identical or 1 for dissimilar molecules. The  $\gamma(i_{max})^{AB,C}$  parameter defines the fraction of collisions that will have sufficient energy to dissociate. Taking  $i$  as the pre-collision vibrational state of the dissociating molecule, the result is

$$\mathcal{Y}(i_{max})^{AB,C} = \sum_{i=0}^{i_{max}-1} \frac{1}{z_v(T)^{AB}} \left[ Q\left(\frac{5}{2} - \omega^{AB,C}, \left(\frac{(i_{max}-i)\theta_v^{AB}}{T}\right)\right) \exp\left(\frac{-i\theta_v^{AB}}{T}\right) \right], \quad (11)$$

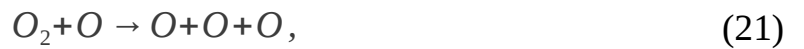
where  $Q(a, x) = \Gamma(a, x) / \Gamma(a)$  is a form of the incomplete Gamma function and  $z_v(T)^{AB} = 1/[1 - \exp(-\theta_v/T)]$  is the vibrational partition function [1].

### 2.3.1 Dissociation in *dsmcFoam*

We have implemented Q-K dissociation reactions in *dsmcFoam* for the following nine molecule-molecule dissociations, which we term “Type I” dissociations:



and the following six molecule-atom dissociations, or “Type II” dissociations







We consider dissociation reactions for two cases involving either thermochemical equilibrium or non-equilibrium. For the case of equilibrium, if a DSMC particle meets the criterion for dissociation to occur (Equation 8) then we may simply update a counter within our DSMC simulation during which no particle splitting takes place. This procedure enables reaction rates to be calculated at a constant temperature for a gas in equilibrium and then compared to the analytical Q-K solution of Equation (9). In his 2011 Q-K paper [1], Bird does not present any DSMC simulation data: it is solely analytical work with a description of the DSMC procedure for each reaction. Gallis *et al.* [2] and Wysong *et al.* [19] have presented some DSMC simulation data, however this work was performed using a DSMC implementation for exchange reactions that has since been superseded.

For the non-equilibrium case, particle splitting may occur and nascent species are introduced with the associated conservation of mass, momentum and energy. This procedure gives rise to an initial non-equilibrium mixture which eventually settles down to steady-state, thermochemical equilibrium. For the non-equilibrium case the results from the *dsmcFoam* Q-K implementation are compared with analytical solutions. The analytical results are generated for the simultaneous solution of rate kinetic equations describing the time evolution of the concentration of each chemical species as well as the equilibrium temperature of the reacting gas mixture [20]. The overall rate of change of the concentration of species  $s$  is given by the summation over all individual rate processes of the form:

$$\frac{d[X_s]}{dt} = -k_f[X_s][X_r] + k_b[X_{p1}][X_{p2}], \quad (27)$$

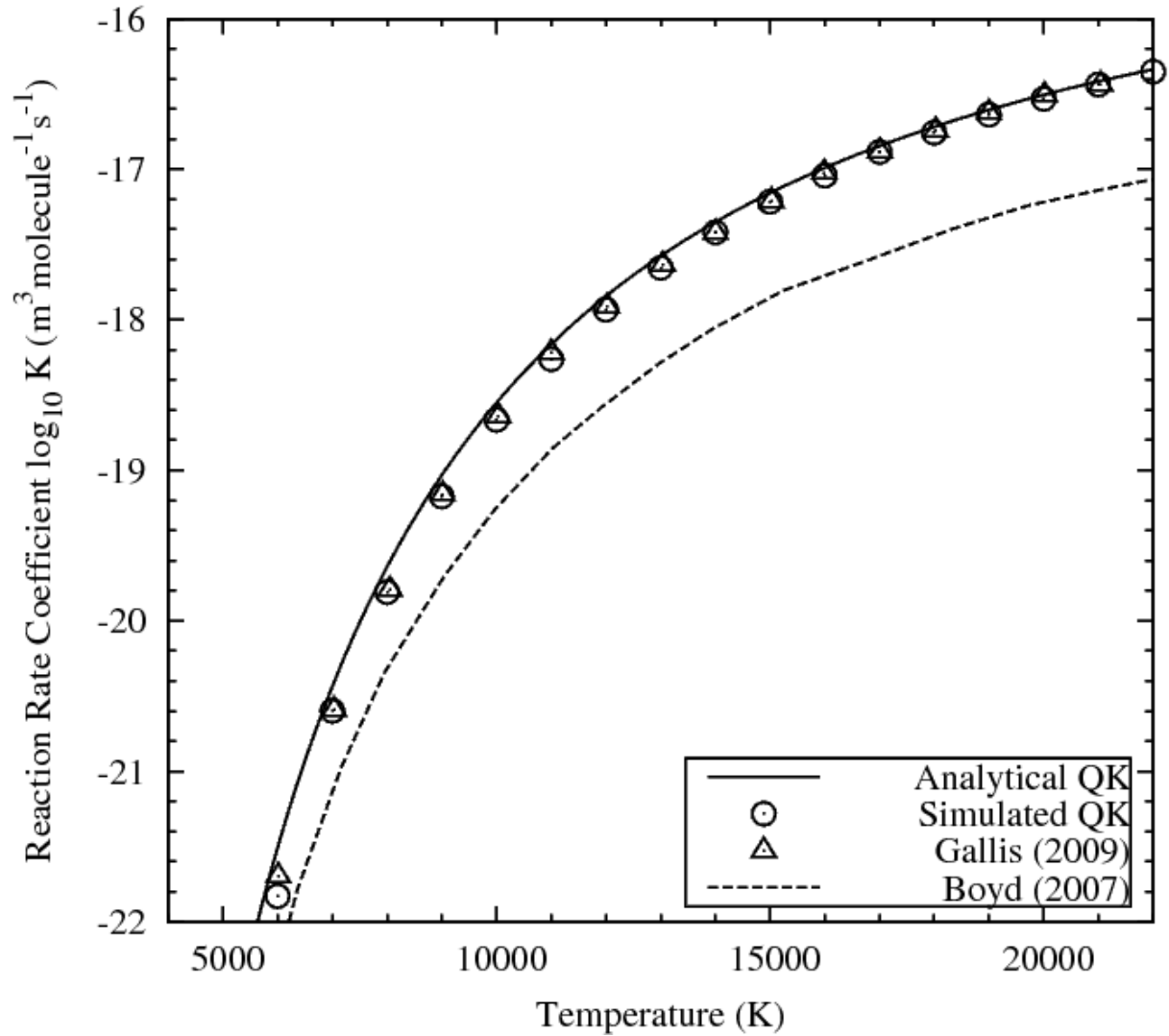
where  $k_f$  and  $k_b$  are forward and backward rate coefficients,  $X_r$  is a reactant species, and  $X_{p1}$  and  $X_{p2}$  are product species. The forward reaction only is considered and backward recombination is deactivated. The  $k_f$  is determined from the equilibrium Q-K rate (Equation 9) and is set in Arrhenius form as shown in Table 1. A system of five equations is solved simultaneously for species  $N_2$ ,  $O_2$ ,  $NO$ ,  $N$ , and  $O$  for high-temperature air. The overall energy balance is also analysed accounting for the internal energy modes (translation, rotation, vibration) and chemical reactions in order to determine the equilibrium temperature.

### 2.3.2 Equilibrium dissociation

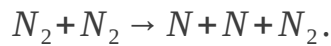
Adiabatic box simulations are performed to measure the equilibrium dissociation rate coefficients for each reaction. A single cubic cell of side length  $1 \times 10^{-5}$  m, with six specularly reflective surfaces, was used for this purpose. Following the work of Haas [21], a total of 50,000 DSMC particles were used in each simulation, a time step size of  $1.52 \times 10^{-9}$  s was adopted, and the rotational and vibrational collision numbers were set to 1. The particles were allowed to move and exchange energy but no particle splitting occurred. Only the forward reaction was considered during the reaction, and recombination was discounted.

Figure 4 shows the equilibrium reaction rate coefficients for the Type I dissociation reaction defined by Equation (13), i.e. dissociation of a nitrogen molecule in a collision with another nitrogen molecule. The analytical and numerical Q-K solutions are in satisfactory agreement, while the *dsmcFoam* Q-K values remain in excellent agreement with the DSMC results of Gallis *et al.* [2], thus verifying the *dsmcFoam*

implementation of the Q-K approach for dissociation. In comparison with the TCE results of Boyd [18] the Q-K values show a similar trend, however there is a discordance in the level of agreement and higher Q-K values are predicted.



**Figure 4** Equilibrium dissociation rate coefficient for Type I dissociation,



Although not presented in this paper for reasons of conciseness, the remaining Type I and Type II dissociation reactions have been implemented in *dsmcFoam* and these demonstrate similar levels of agreement to those shown in Figure 4 when compared

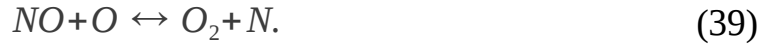
with the Q-K analytical rates, the Gallis *et al.* [2] DSMC results and Boyd's [18] TCE rates.

## 2.4 Exchange reactions

An exchange reaction comprises one stable molecule and one radical before and after the reaction occurs. These reactions take the form  $A+B \leftrightarrow C+D$ , where  $A$  and  $C$  are molecules, and  $B$  and  $D$  are atoms. In the 5-species air model considered in this paper, there are two sets of exchange reactions:



and



Each of these has a forward (endothermic) and a backward (exothermic) direction resulting in a total of four exchange reactions.

The DSMC implementation of exchange chemistry leads to reactions being possible if the collision energy  $E_c$  is greater than the activation energy  $E_a$ , with a probability of

$$P = \left(1 - \frac{E_a}{E_c}\right)^{3/2-\omega} / \sum_{i=0}^{i_{max}} \left(1 - \frac{i k \theta_v}{E_c}\right)^{3/2-\omega}. \quad (30)$$

The summation in the denominator can be taken as unity when  $E_a/k < \theta_v$  and the analytical Q-K rates given by Bird [1] are

$$k_f(T) = R_{coll}^{A,B} \exp\left(\frac{E_a^{A,B}}{kT}\right) / z_v(T)^A, \quad (31)$$

and

$$k_r(T) = R_{coll}^{C,D} \exp\left(\frac{E_a^{C,D}}{kT}\right) / z_v(T)^C, \quad (32)$$

where  $k_f(T)$  and  $k_r(T)$  are the forward and reverse reaction rates, respectively,  $z_v(T)$  is the vibrational partition function, and  $R_{coll}$  is the collision rate between the species indicated in the superscript and is given by Equation (10).

The default activation energy for the forward exchange reactions is the heat of reaction,  $E_r$ , and for the reverse reaction it is zero. The activation energies and heats of formation for the four exchange reactions are shown in Table 1 (reaction numbers 16 to 19).

In order to ensure that the ratio of the number of forward to reverse exchange reactions is consistent with that predicted by statistical mechanics it is necessary to adjust the activation energies in a phenomenological manner. For forward exchange reactions, the adjusted activation energy  $E'_{a,f}$  is

$$E'_{a,f} = |E_h| \left[ 1 + a \left( \frac{T}{273} \right)^b \right], \quad (33)$$

and for the reverse exchange reaction it is

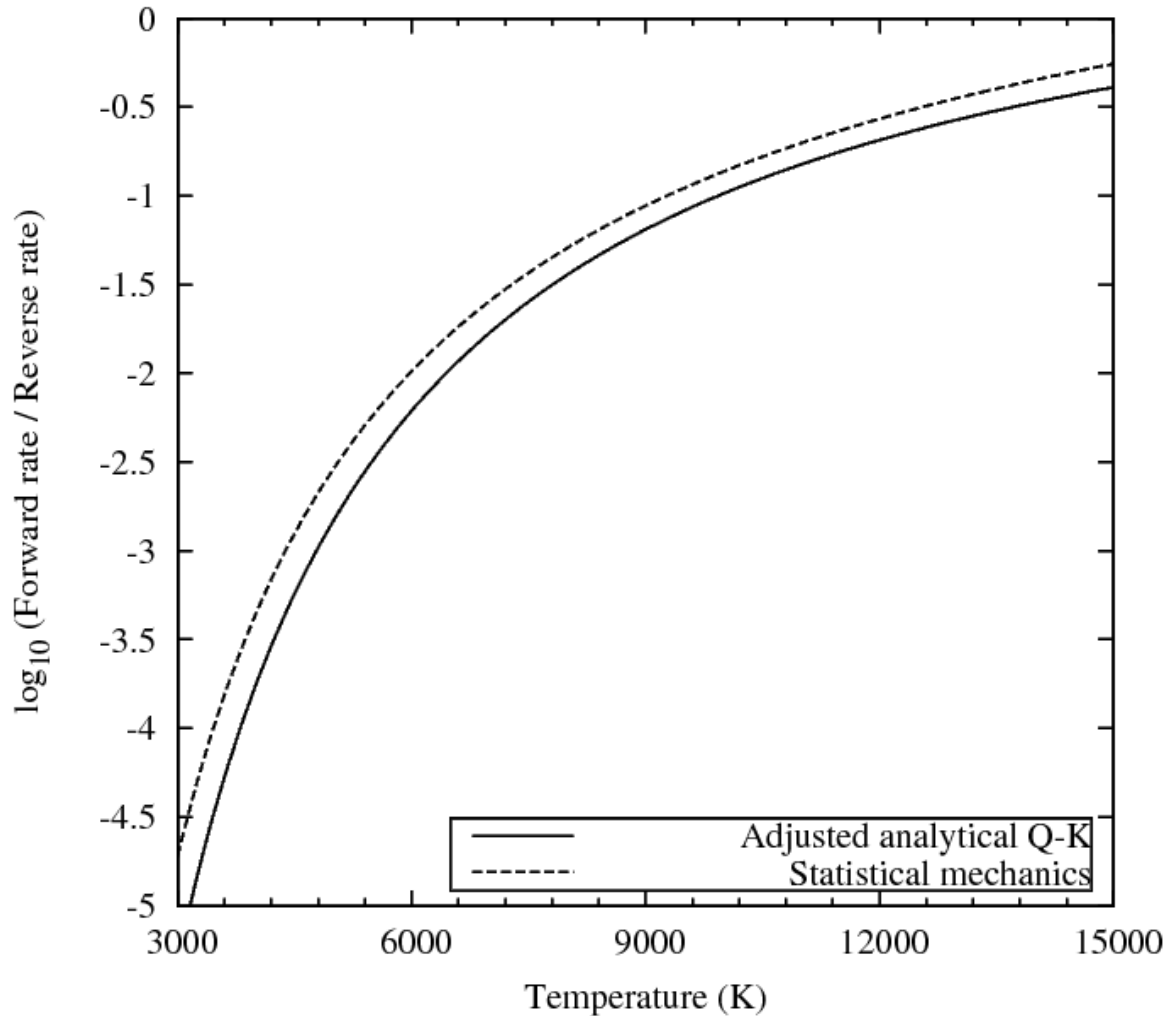
$$E'_{a,r} = |E_h| \left[ a \left( \frac{T}{273} \right)^b \right], \quad (34)$$

where  $|E_h|$  is the modulus of the heat of formation (see Table 1) and  $a$  and  $b$  are adjustable parameters.

**Table 1** *Parameters for adjusted activation energies in Equations (33) and (34).*

| <i>Exchange reaction</i> | <i>a</i> | <i>b</i> |
|--------------------------|----------|----------|
| $NO+O \rightarrow O_2+N$ | 0.085    | 0.65     |
| $O_2+N \rightarrow NO+O$ | 0.1      | 0.1      |
| $N_2+O \rightarrow NO+N$ | 0.15     | 0.15     |
| $NO+N \rightarrow N_2+O$ | 0.033    | 0.8      |

In our *dsmcFoam* implementation, we have chosen values of  $a$  and  $b$  for the four exchange reactions that enable our DSMC results to be in satisfactory agreement with both the analytical equilibrium Q-K rates of Equations (31) and (32), and the analytical non-equilibrium rates predicted by Equation (27), and, finally, to ensure that the ratio of the forward to reverse reactions is consistent with that predicted by statistical mechanics [1]. The parameters  $a$  and  $b$  are given in Table 1 and were determined using Bird's QKRates program [22]. Figure 5 shows the ratio of forward to reverse exchange reaction rate for  $N_2+O \leftrightarrow NO+N$ . and reasonable agreement is found in comparison with the equilibrium constant from statistical mechanics [22].



**Figure 5** The forward to reverse rate ratio for  $N_2 + O \leftrightarrow NO + N$ .

It should be noted that the equilibrium parameters  $a$  and  $b$  may be chosen such that both curves in Figure 5 are identical, however, compromise values were selected in order to obtain optimum agreement also with Equations (27), (31) and (32) as explained previously.

#### 2.4.1 Equilibrium exchange

Adiabatic box simulations are performed to measure the equilibrium rate coefficients

for two of the exchange reactions shown in Table 1. The cases have set-up parameters identical to those for the equilibrium dissociation reactions presented in Section 2.3.2, and a 50% split of each species by number is used as the initial conditions.

Figure 6 shows the equilibrium reaction rate for the forward endothermic exchange reaction  $NO+O \rightarrow O_2+N$ . The TCE rate from Ref. [18], the DSMC data from Gallis *et al.* [2], and a rate representative of the National Institute of Standards and Technology (NIST) database [23] are also included. In addition to these, the *dsmcFoam* implementation for exchange has been calculated using two different definitions for temperature in Equations (33) and (34), these being the macroscopic and the collision temperature. The collision temperature has been used for all *dsmcFoam* calculations in this paper and its definition is [1]:

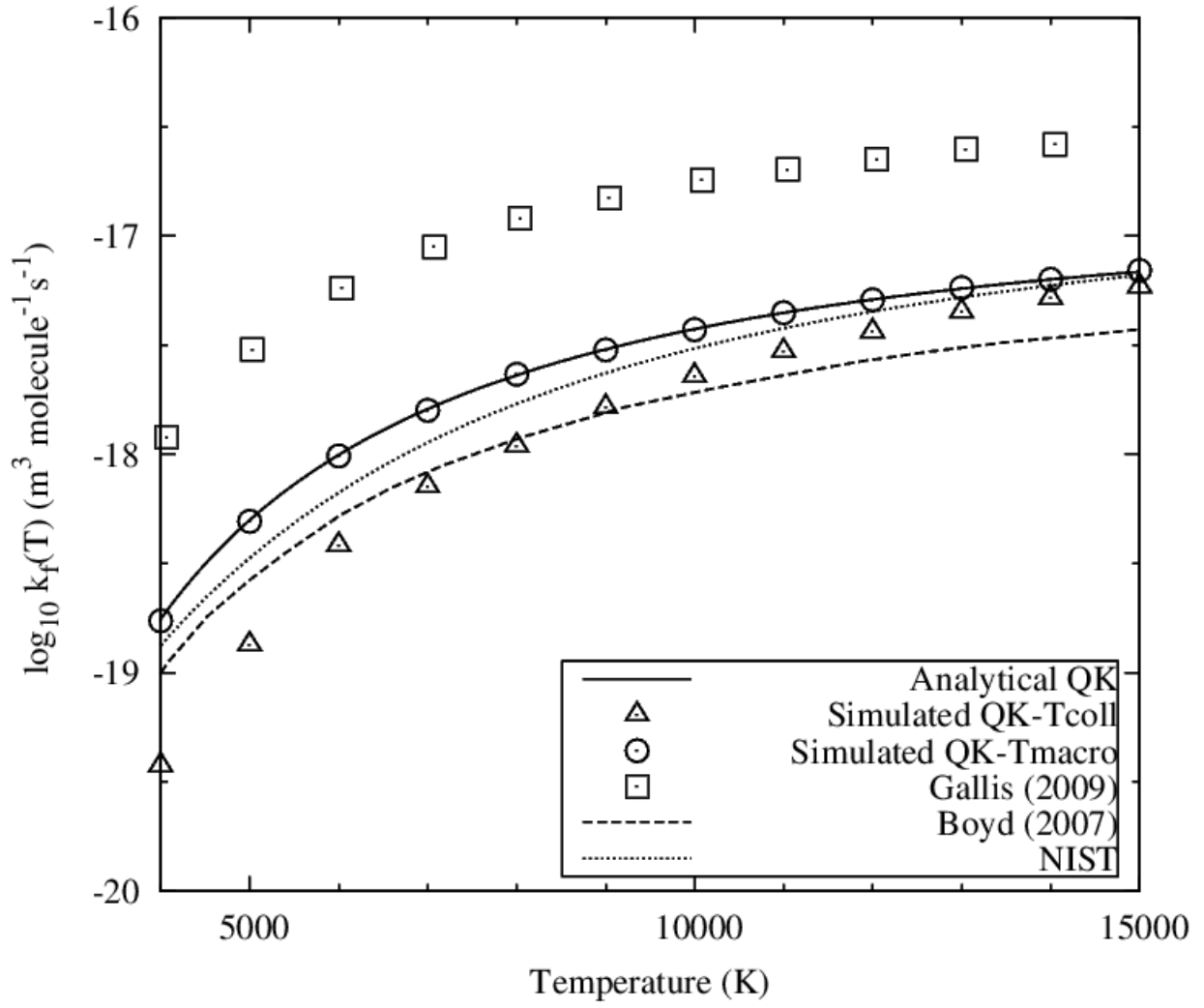
$$T_{coll} = \left( m_r^{A,B} c_r^2 / (2k) \right) / (5/2 - \omega^{A,B}). \quad (35)$$

In his 2011 paper Bird [1] recommends that if the collision temperature is to be used then the exchange factor  $a$  in Equations (33) and (34) needs to be replaced by:

$$a' = \left[ (5/2 - \omega^{A,B})^b \Gamma(5/2 - \omega^{A,B}) / \Gamma(5/2 - \omega^{A,B} + b) \right] a \quad (36)$$

This step was considered necessary due to the inequality of macroscopic and collision temperatures when the parameter  $b$  is not equal to zero or unity. However, our *dsmcFoam* calculations for exchange showed no apparent difference whether  $T_{coll}$  was used in tandem with Equation (36) or not. It is desirable that the collision temperature be used in DSMC procedures rather than the macroscopic value as information should be passed upwards from the molecular level.





**Figure 6** Forward endothermic equilibrium exchange rate coefficient for  $\text{NO} + \text{O} \rightarrow \text{O}_2 + \text{N}$ .

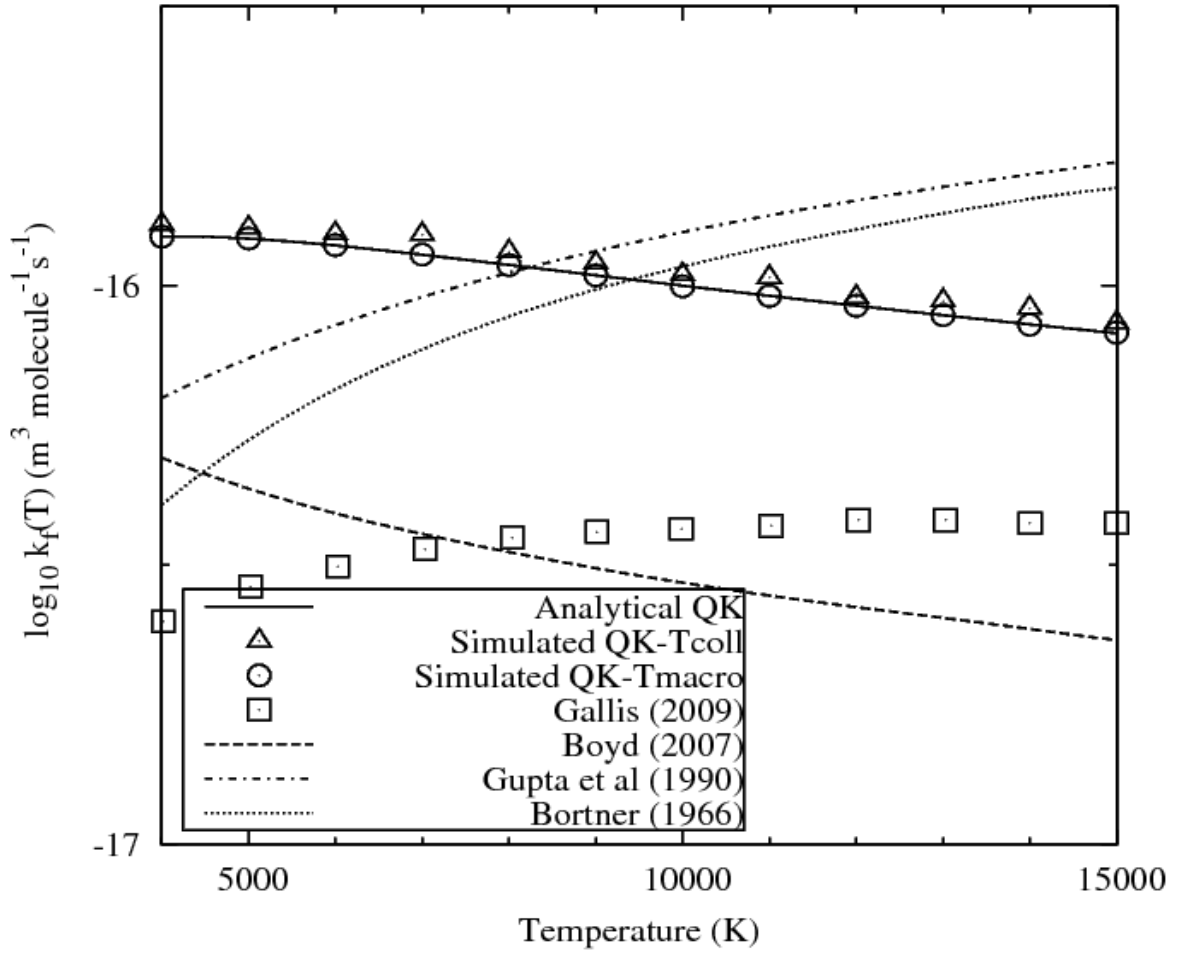
In any case, it is clear from all our figures for exchange reactions that the use of macroscopic temperature in our *dsmcFoam* implementation produces equilibrium rates that match the Q-K analytical values. Such a result helps verify our coding, however the application of the collision temperature for exchange does produce results which are highly sensitive to the choice of the exponent parameter  $b$  in Equations (33) and (34). Averaging over all collisions  $\bar{T}_{\text{coll}} = \bar{T}_{\text{macro}}$ , however,

$\bar{T}_{coll}^b \neq \bar{T}_{macro}^b$  unless  $b = 1$  or  $0$  (note, the over bar represents average quantities).

This can explain why there is closer agreement between the exchange rates found using  $T_{coll}$  and  $T_{macro}$  in Figure 7, as they use small values of the exponent  $b$  whereas there is an increased disparity between the  $T_{coll}$  and  $T_{macro}$  rates in Figure 6 a larger value of  $b$  is employed.

The simulated Q-K rates using  $T_{coll}$  are seen in Figure 6 to fall within the range covered by the TCE and the NIST rates for temperatures in excess of around 7000 K. It is interesting to note that the Gallis *et al.* [2] data, based on a DSMC implementation which did not consider the adjustment of activation energies, shows consistently higher reaction rates across the range of temperatures considered.

The corresponding reverse exothermic equilibrium rate for the  $O_2 + N \rightarrow NO + O$  exchange reaction is shown in Figure 7. Additional experimental data from Gupta *et al.* [24] and Bortner [25] have been included. Close agreement is observed between the Q-K rates predicted by the collision and macroscopic temperatures because the coefficient  $b$  is small (0.1) for this reaction. The trend of decreasing reaction rate with temperature is similar for both Q-K and TCE, however the Q-K rates are higher across the range of temperatures studied and are closer of the results of Gupta *et al.* and Bortner. In comparison with the activation energy-adjusted Q-K approach presented in this paper, the previous incarnation of Q-K considered by Gallis *et al.* predicts lower rates for this reaction with their results being closer to the TCE rates. A similar level of agreement was found for the forward and reverse equilibrium rates for the  $N_2 + O \rightarrow NO + N$  reaction.



**Figure 7** Reverse exothermic equilibrium exchange rate coefficient for  $\text{O}_2 + \text{N} \rightarrow \text{NO} + \text{O}$ .

## 2.5 Non-equilibrium dissociation and exchange in air

Unlike the equilibrium rate calculations shown previously, the non-equilibrium dissociation and exchange reactions presented in this section involve particle splitting. The physical dissociation or exchange of the molecules is accompanied by a process of detailed balance for mass, momentum and energy as DSMC particles disintegrate or exchange.

The complete set of 19 reactions shown in Table 2 is considered in an adiabatic box filled with air at 0.063 *atm* pressure at an initial composition of 79%  $N_2$  and 21%  $O_2$  and temperature of 30,000 K. Other simulation parameters are identical to those described in section 2.3.2. A single cell adiabatic cube of side length  $1 \times 10^{-5}$  m is again employed, and 50,000 initial DSMC particles were used with a time-step of  $1.52 \times 10^{-9}$  s. The fate of each species is measured in a transient manner as the reaction proceeds from equilibrium initial conditions, through a non-equilibrium reaction process to a final state approaching equilibrium. Once again, the backward recombination reaction has been deactivated and only the forward chemistry is dealt with. For internal energy exchange both the rotational and vibrational collision numbers have been fixed at 1. The *dsmcFoam* Q-K results are compared with the analytical solution provided by Equation (27). The forward rate coefficient  $k_f(T)$  for Equation (27) is provided as a best-fit Arrhenius curve to the equilibrium analytical Q-K data, while the Arrhenius rate takes the form:

$$k_f(T) = C_1 T^{(C_2)} \exp\left(\frac{-E_a}{kT}\right), \quad (37)$$

where  $k$  is the Boltzmann constant,  $C_1$  and  $C_2$  are reaction-specific constants, and  $E_a$  is the activation energy, the values of which are provided in Table 1.

Figures 8 and 9 show the evolution of species and overall temperature, respectively.. The species concentrations at any instant in time ( $n_s^t$ ) have been non-dimensionalised with respect to the the initial number density of the species ( $n^0$ ). In general, the Q-K predictions of the constituent evolution agree well with the analytical result although there is an under-prediction of *NO* towards the end of the reactions. Oxygen scatter towards the tail of the reaction is due to its rapid depletion

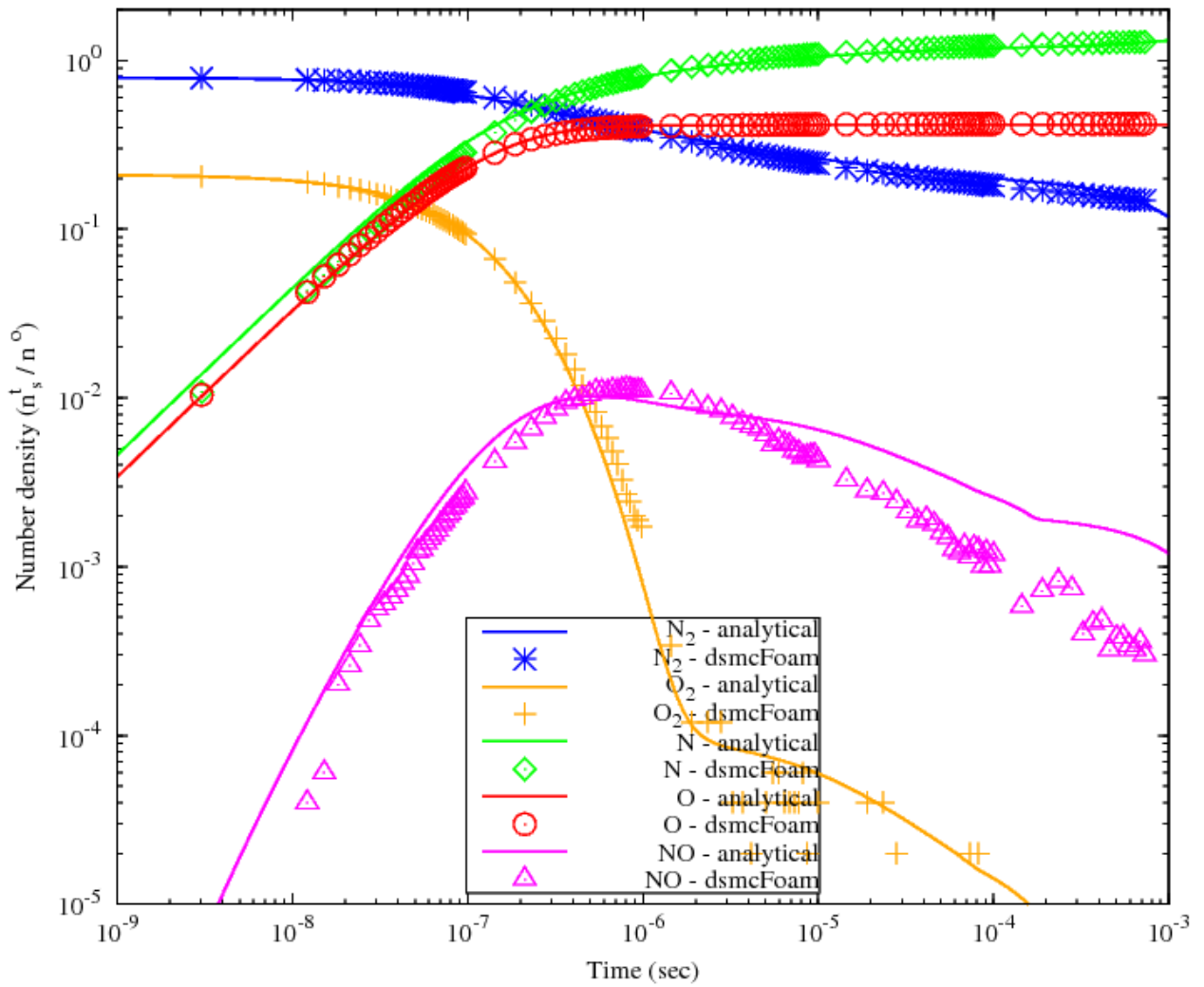
as the reactions progress. Considering the overall temperature field for the gas mixture, very good agreement between the DSMC and analytical solutions is evident for each case, with any scatter being explained by the extinction of the  $O_2$  and  $NO$  molecules towards the end of the reaction process.

These results highlight the important role that endothermic dissociation plays in acting as an energy sink in hypersonic reacting flows. The energy redistribution during the chemical reaction manifests itself as a reduction in the enthalpy of the flow, with a consequent reduction in surface heat transfer to the hypersonic body.

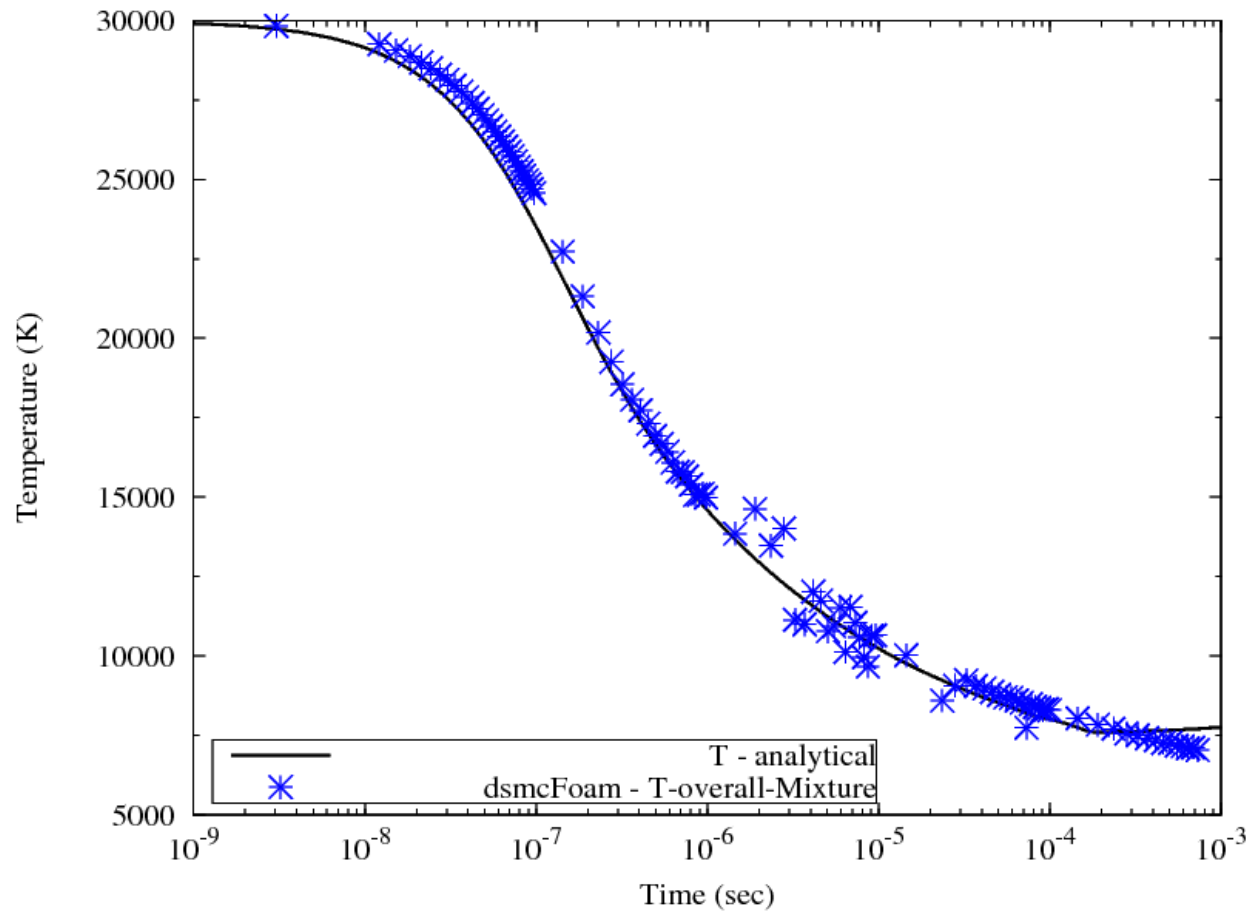
**Table 2** Chemical reaction list and equivalent Arrhenius rate variables for the 5-species air model in dsmcFoam.

| No. | Reaction                            | Heat of formation<br>$\times 10^{19} \text{ J}$ | $C_1$                  | $C_2$ | Activation energy<br>$E_a$<br>$\times 10^{19} \text{ J}$ |
|-----|-------------------------------------|---|------------------------|-------|--|
| 1   | $O_2 + N \rightarrow O + O + N$     | 8.197   | $1.1 \times 10^{-10}$  | -1.0  | 8.197  |
| 2   | $O_2 + NO \rightarrow O + O + NO$   | 8.197   | $1.1 \times 10^{-10}$  | -1.0  | 8.197  |
| 3   | $O_2 + N_2 \rightarrow O + O + N_2$ | 8.197   | $1.3 \times 10^{-10}$  | -1.0  | 8.197  |
| 4   | $O_2 + O_2 \rightarrow O + O + O_2$ | 8.197   | $5.33 \times 10^{-11}$ | -1.0  | 8.197  |
| 5   | $O_2 + O \rightarrow O + O + O$     | 8.197   | $1.5 \times 10^{-10}$  | -1.05 | 8.197  |
| 6   | $N_2 + O \rightarrow N + N + O$     | 15.67   | $4.0 \times 10^{-12}$  | -0.54 | 15.67  |
| 7   | $N_2 + O_2 \rightarrow N + N + O_2$ | 15.67   | $1.5 \times 10^{-11}$  | -0.68 | 15.67  |
| 8   | $N_2 + NO \rightarrow N + N + NO$   | 15.67   | $1.5 \times 10^{-11}$  | -0.68 | 15.67  |
| 9   | $N_2 + N_2 \rightarrow N + N + N_2$ | 15.67   | $4.1 \times 10^{-12}$  | -0.62 | 15.67  |
| 10  | $N_2 + N \rightarrow N + N + N$     | 15.67   | $1.0 \times 10^{-11}$  | -0.68 | 15.67  |
| 11  | $NO + N_2 \rightarrow N + O + N_2$  | 10.43   | $2.1 \times 10^{-10}$  | -1.0  | 10.43  |
| 12  | $NO + O_2 \rightarrow N + O + O_2$  | 10.43   | $2.0 \times 10^{-10}$  | -1.0  | 10.43  |

|    |                                  |        |                       |       |       |
|----|----------------------------------|--------|-----------------------|-------|-------|
| 13 | $NO + NO \rightarrow N + O + NO$ | 10.43  | $1.0 \times 10^{-10}$ | -1.0  | 10.43 |
| 14 | $NO + O \rightarrow N + O + O$   | 10.43  | $4.0 \times 10^{-10}$ | -1.1  | 10.43 |
| 15 | $NO + N \rightarrow N + O + N$   | 10.43  | $4.0 \times 10^{-10}$ | -1.1  | 10.43 |
| 16 | $NO + O \rightarrow O_2 + N$     | 2.719  | $2.3 \times 10^{-19}$ | 0.50  | 2.719 |
| 17 | $N_2 + O \rightarrow NO + N$     | 5.175  | $0.8 \times 10^{-16}$ | 0     | 5.175 |
| 18 | $O_2 + N \rightarrow NO + O$     | -2.719 | $4.0 \times 10^{-15}$ | -0.39 | 0.2   |
| 19 | $NO + N \rightarrow N_2 + O$     | -5.175 | $5.0 \times 10^{-16}$ | -0.35 | 0.2   |



**Figure 8** Species concentrations during the decomposition of air from an initial temperature of 30,000 K and pressure of 0.063 atm.



**Figure 9** Overall temperature evolution of the gas mixture during the decomposition of air from an initial temperature of 30,000 K and pressure of 0.063 atm.

### 3.0 A hypersonic flow test case

In order to test the *dsmcFoam* implementation of the Q-K chemistry model in a practical scenario a hypersonic flow test case is simulated. This consists of high speed, rarefied air flow over a 2D cylinder at the atmospheric free stream conditions shown in Table 3.

**Table 3** *Free stream conditions for test case of hypersonic air cross flow over a 2D cylinder.*

|                                     |                                       |
|-------------------------------------|---------------------------------------|
| <i>Cylinder diameter</i>            | 2 m                                   |
| <i>Flow velocity</i>                | 6813 m/s                              |
| <i>Free stream temperature</i>      | 187 K                                 |
| <i>Cylinder wall temperature</i>    | 1000 K                                |
| <i>N<sub>2</sub> number density</i> | $1.13 \times 10^{20} \text{ m}^{-3}$  |
| <i>O<sub>2</sub> number density</i> | $3.031 \times 10^{19} \text{ m}^{-3}$ |

These conditions correspond to the Earth's atmosphere at 86 km altitude and a Mach number of 24.85. The cylinder walls are fully diffuse, and all 19 chemical reactions shown in Table 2 are activated. Comparisons are made with the equivalent solution using the established DSMC code MONACO which employs TCE chemistry. In all cases the rotational and vibrational collision numbers are set to 5 and 50, respectively, and the TCE Arrhenius rates for dissociation and exchange are provided from the Q-K analytical equilibrium values, using Equation 9 for dissociation and Equations (33) and (34) for exchange. The mesh size for the *dsmcFoam* study is 240,000 cells with a time-step fixed at  $1 \times 10^{-7} \text{ s}$  and, following particle sensitivity trials, there were 23.4 million DSMC particles in the system at steady-state. For the MONACO study the domain contains 175,000 cells with automatic sub-cell generation and the total number of DSMC particles at steady-state is 37.5 million. In addition, cell-based,



variable time-steps are used such that the ratio of the time step to mean collision time in each cell is approximately 0.2. We suggest that this test case be considered as a reference 2D benchmark trial for future DSMC chemistry implementations.

Comparative tests between *dsmcFoam* and MONACO for non-reacting conditions showed excellent agreement between the aerothermodynamic quantities as demonstrated in Figure 10 which shows the temperature profile along the stagnation streamline. Figures 11 to 13 show the reacting flow comparisons between the DSMC codes for velocity, density and temperature, respectively, along the stagnation streamline. As the chemical reactions that occur are mainly characterised by endothermicity, the local enthalpy is reduced in comparison to an inert flow and the maximum shock stand-off distance is located at a position approximately 0.36 *m* from the cylinder stagnation point.

Figure 12 shows that the stagnation streamline densities for  $N_2$  and  $NO$  calculated by each code are in relatively close agreement. Although the trends are similar, the values for the atomic species  $N$  and  $O$  predicted with *dsmcFoam* (Q-K) are in excess of those determined by MONACO (TCE). However, the opposite is true for  $O_2$ , with the MONACO (TCE) code producing values exceeding those of *dsmcFoam* (Q-K). The increased number of dissociation events when using Q-K may be qualitatively explained with reference to Wysong *et al.* [19]: the magnitude of the lower level vibrational cross-sections for the Q-K method would mean that more dissociation events are likely, compared with the TCE approach, in non-equilibrium flows with relatively low-vibrational excitation, such as high-altitude re-entry.

Significant reductions in the values of all three temperature modes under reacting flow conditions are evident in Figure 13, with both codes predicting a peak translational temperature along the stagnation streamline of approximately 20,000 K.

This is in contrast to the non-reacting case (Figure 10), for which the peak translational magnitude is approximately 25,000 K. The peak values for rotational and vibrational temperature are also in close agreement, however, the general *dsmcFoam* Q-K temperature values show a small but consistent shift to the left in comparison with the MONACO-based ones. This effect is consistent with the differences in the shock structure indicated by the left-ward velocity-shift shown in Figure 11.

Figures 14 and 15 show the contours of Mach number and *NO* density for each code, respectively. It is clear that the diffuse nature of the shock has been captured by both codes. Although differences exist between the results of the codes for the predicted velocity and temperature fields, it is evident that the local Mach numbers are in close agreement. For the *NO* field it is seen that small differences are evident between the solutions in this qualitative comparison, with the Q-K approach appearing to predict a marginally thinner species layer in the range approaching the peak *NO* values. Nonetheless, the general flow features appear to be similar for both chemistry approaches.

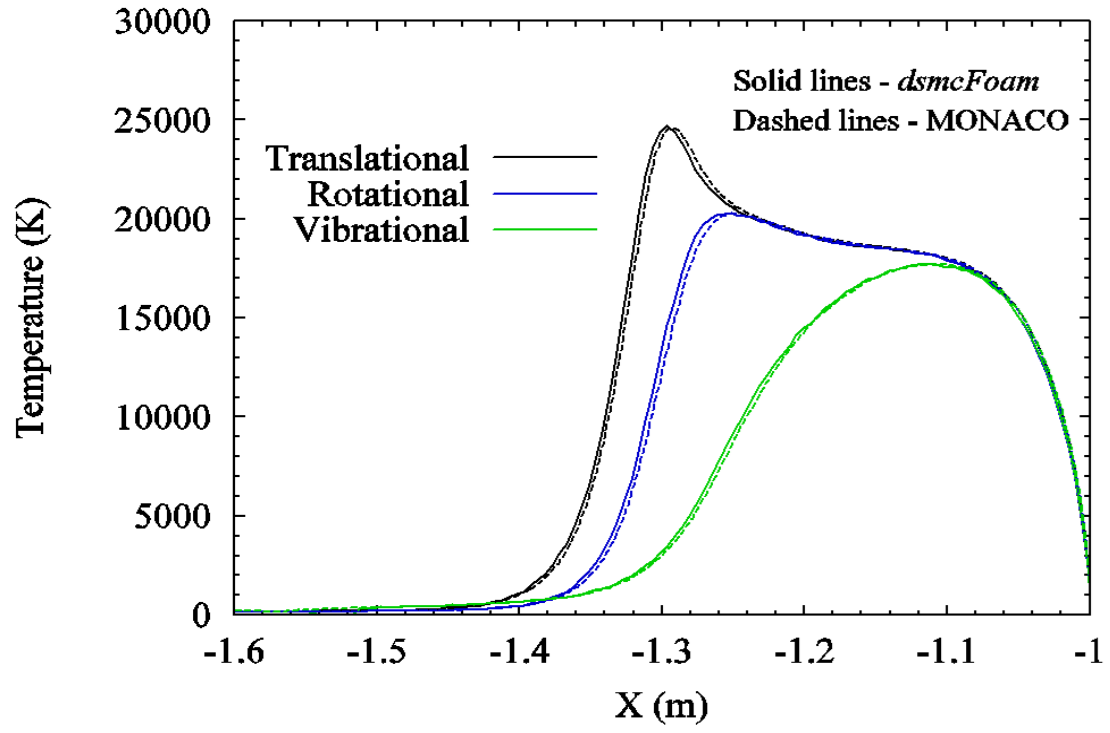
The translational temperature mode is shown in Figure 16 and, in general, a similar qualitative concurrence is evident in all areas of the flow field, with only subtle differences apparent in certain regions.

Finally, the surface properties are shown in Figures 17 and 18. The surface pressure values are in very close agreement between the codes. The peak-value of the heat flux is 64 kW/m<sup>2</sup> for TCE, and 67 kW/m<sup>2</sup> for Q-K. This difference of 4.6 % represents a similar margin to the range of peak-heat fluxes found in a separate case study of non-reacting flow over a 2D cylinder using a variety of DSMC codes [26]. Figures 19 and 20 show the surface temperature-jump and velocity-slip predictions. The general

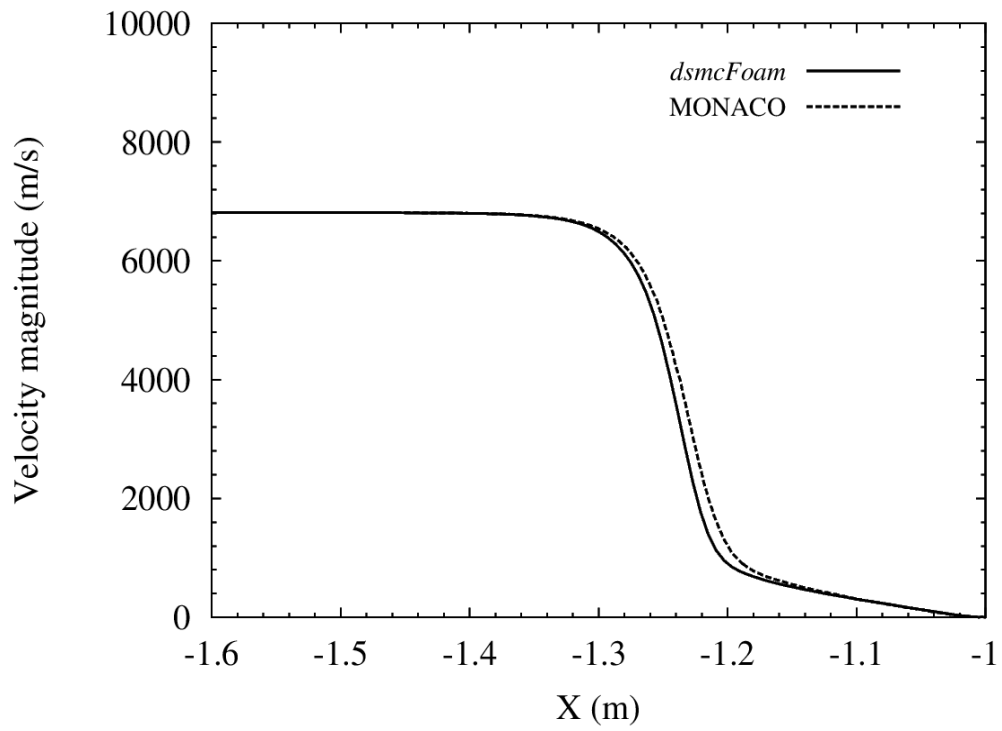
trends are similar for both MONACO and *dsmcFoam*, however, there appears to be a greater level of disparity at some locations on the cylinder surface compared with the results for pressure and heat-flux, with *dsmcFoam* predicting generally higher values of slip and jump.

### 3. Conclusions

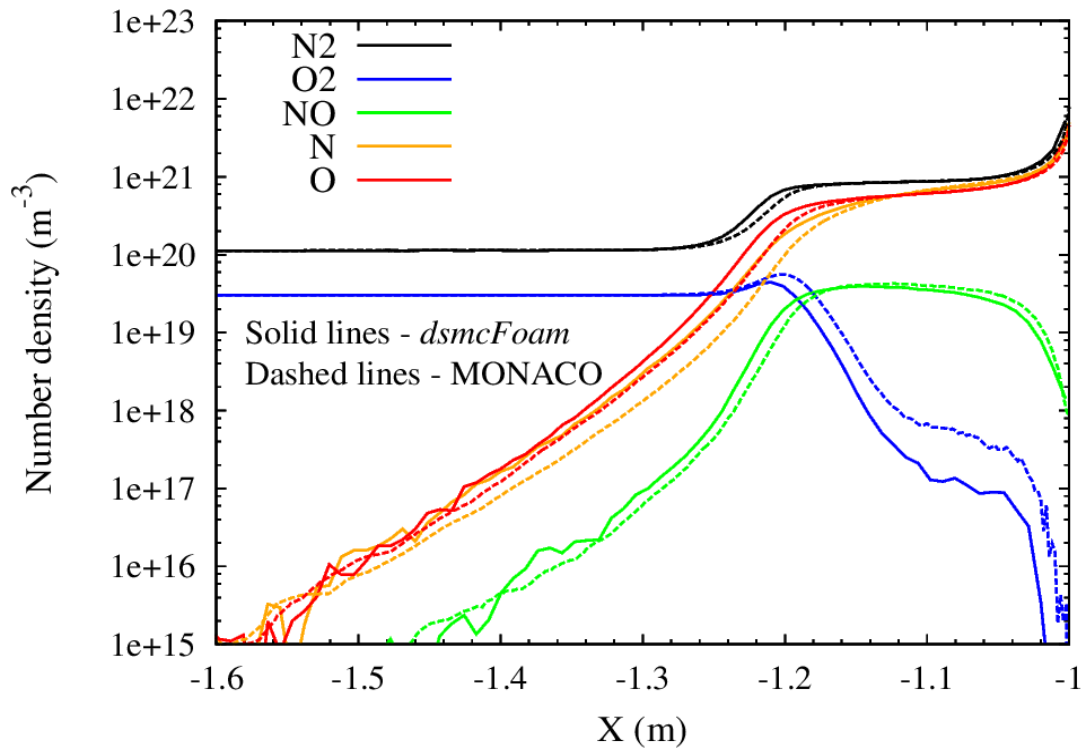
An open source DSMC chemistry model based on the Q-K approach has been developed for use in high-speed, rarefied gas flows. The code, called *dsmcFoam*, has been written within the framework of the open source CFD software suite OpenFOAM. Benchmark test cases demonstrate the successful implementation of the Q-K code into *dsmcFoam* and comparisons with analytical results for dissociation and exchange reactions showed a satisfactory degree of concurrence. Differences in the predicted equilibrium rates for Q-K exchange have been highlighted when macroscopic and collision temperatures are used. New air reaction rates for exchange have been determined, based on the Q-K approach, and presented in Arrhenius form. A test case was run for hypersonic cross flow over a 2D cylinder, and the *dsmcFoam* (Q-K) results were found to be in broad agreement with the established DSMC code MONACO which employs TCE procedures for its reaction modelling. Differences in predicted species profiles along the stagnation streamline for Q-K and TCE have been qualitatively explained. This hypersonic test case is suggested as a reference 2D benchmark trial for future DSMC chemistry implementations.



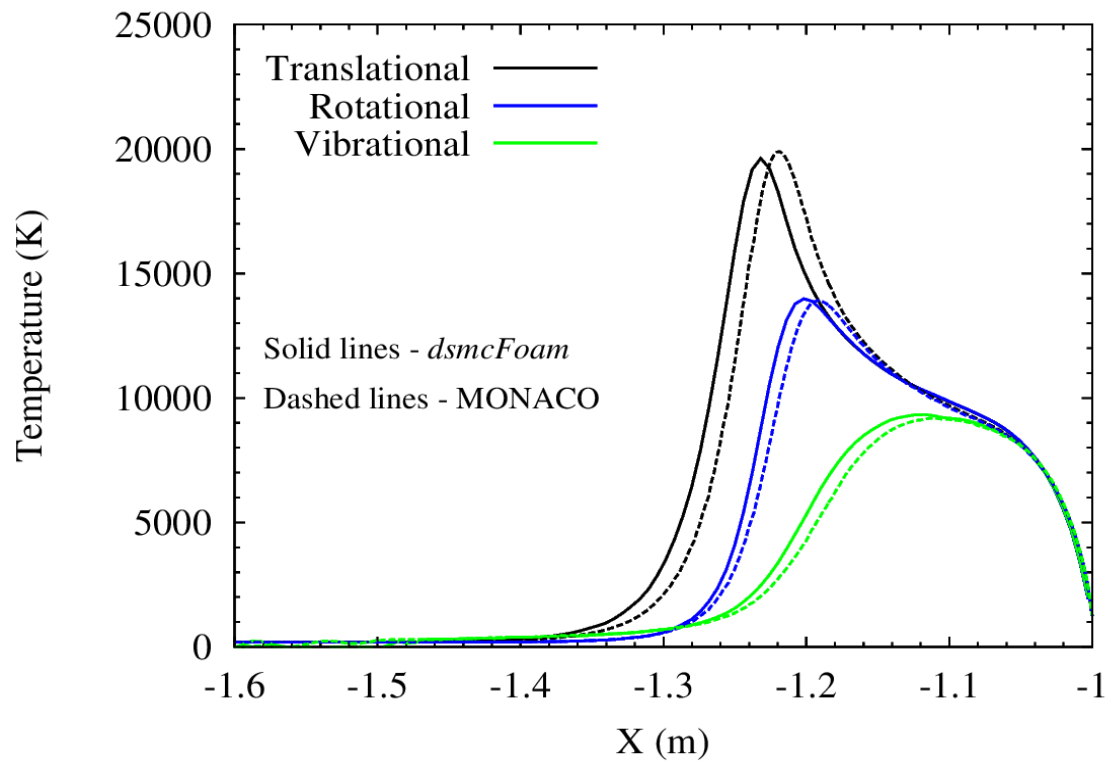
**Figure 10** *Temperature profile along the stagnation streamline for non-reacting air flow over a 2D cylinder.*



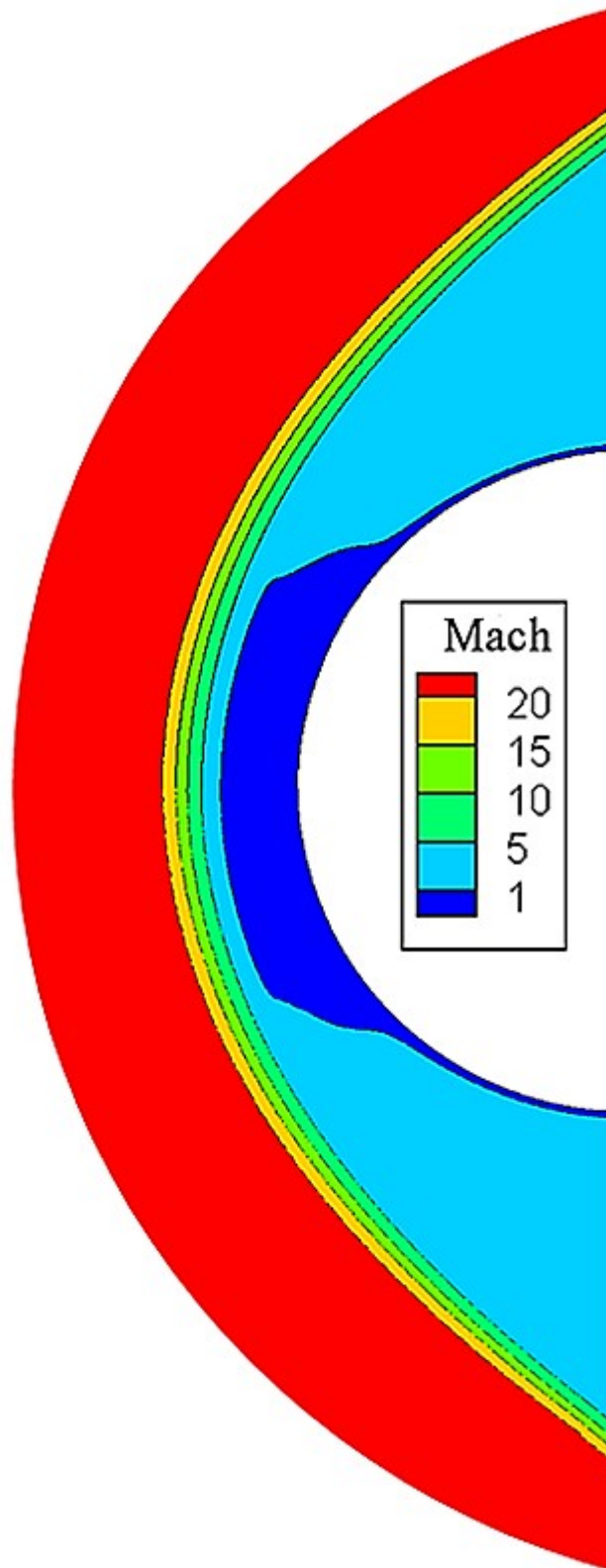
**Figure 11** Velocity profile along the stagnation streamline for reacting air flow over a 2D cylinder.



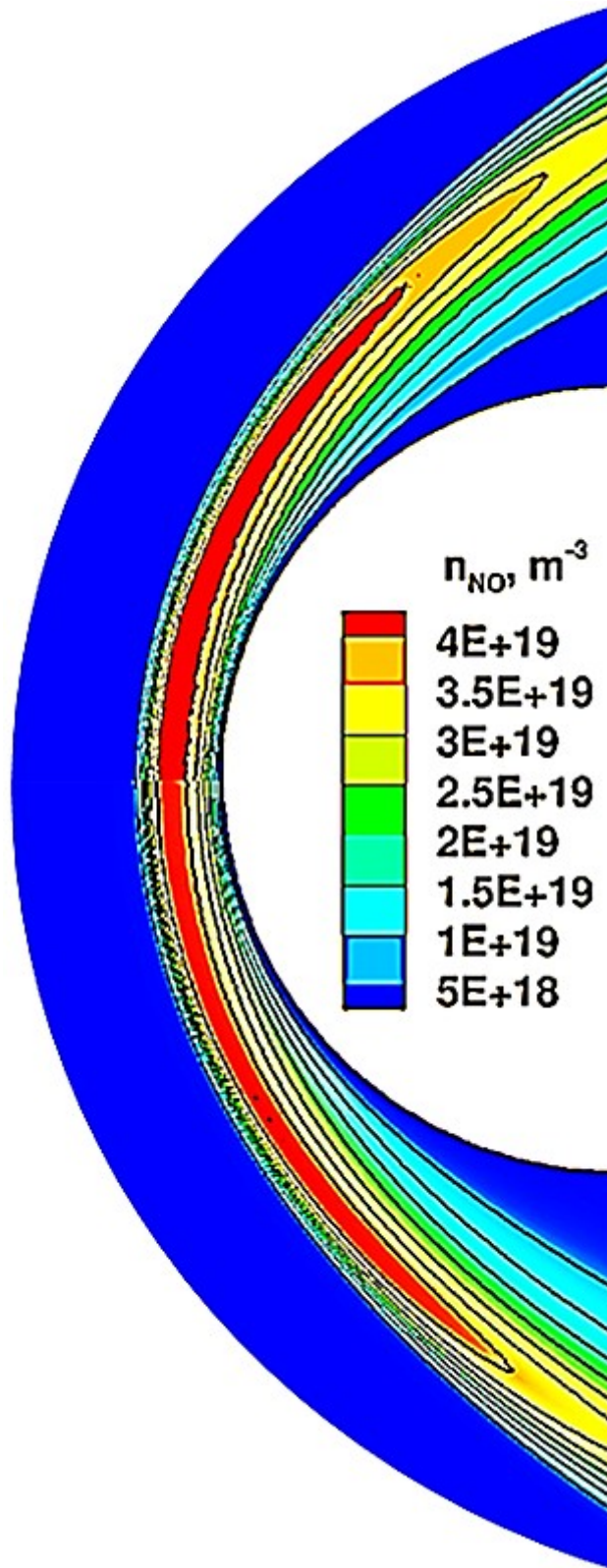
**Figure 12** Number density profile along the stagnation streamline for reacting air flow over a 2D cylinder.



**Figure 13** Temperature profiles along the stagnation streamline for reacting air flow over a 2D cylinder.

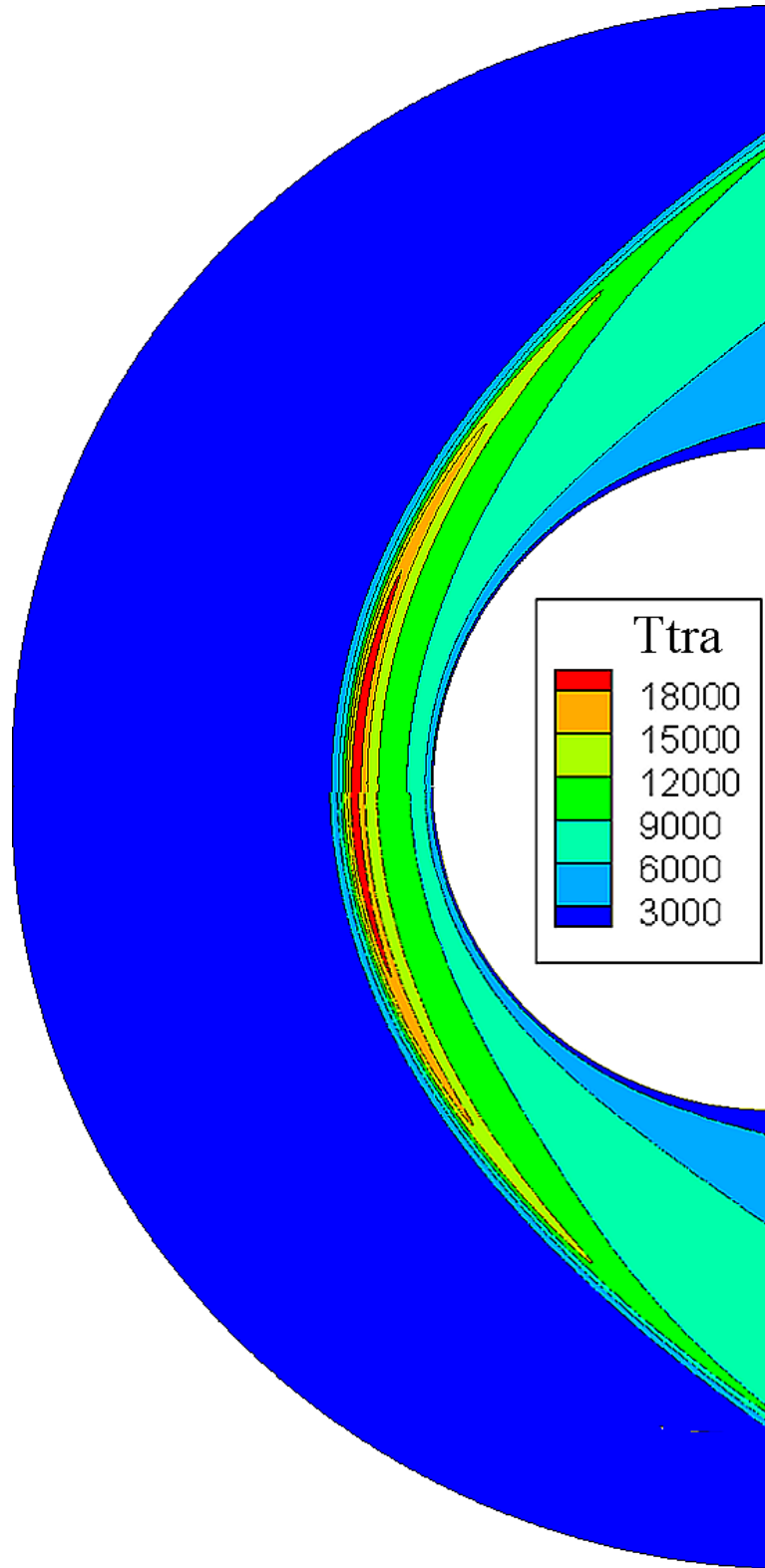


**Figure 14** *Mach number contours predicted using dsmcFoam (Q-K) (lower half) and MONACO (TCE) (upper half) for reacting air flow over a 2D cylinder.*

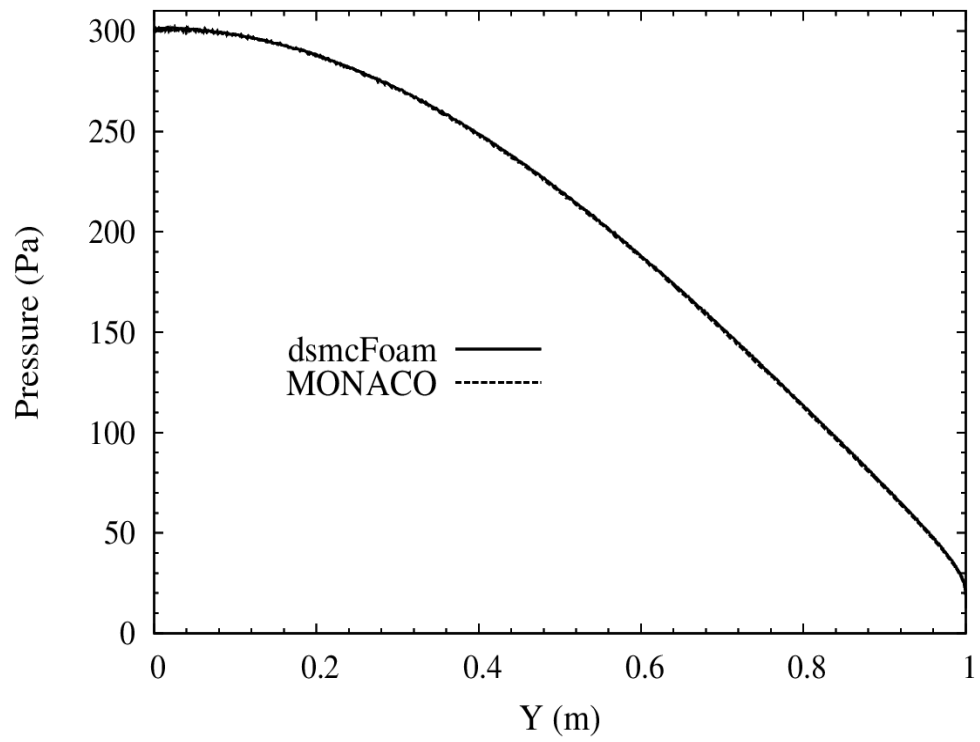


**Figure 15** Contours of NO predicted using dsmcFoam (Q-K) (lower half) and MONACO (TCE) (upper half) for reacting air flow over a 2D cylinder.

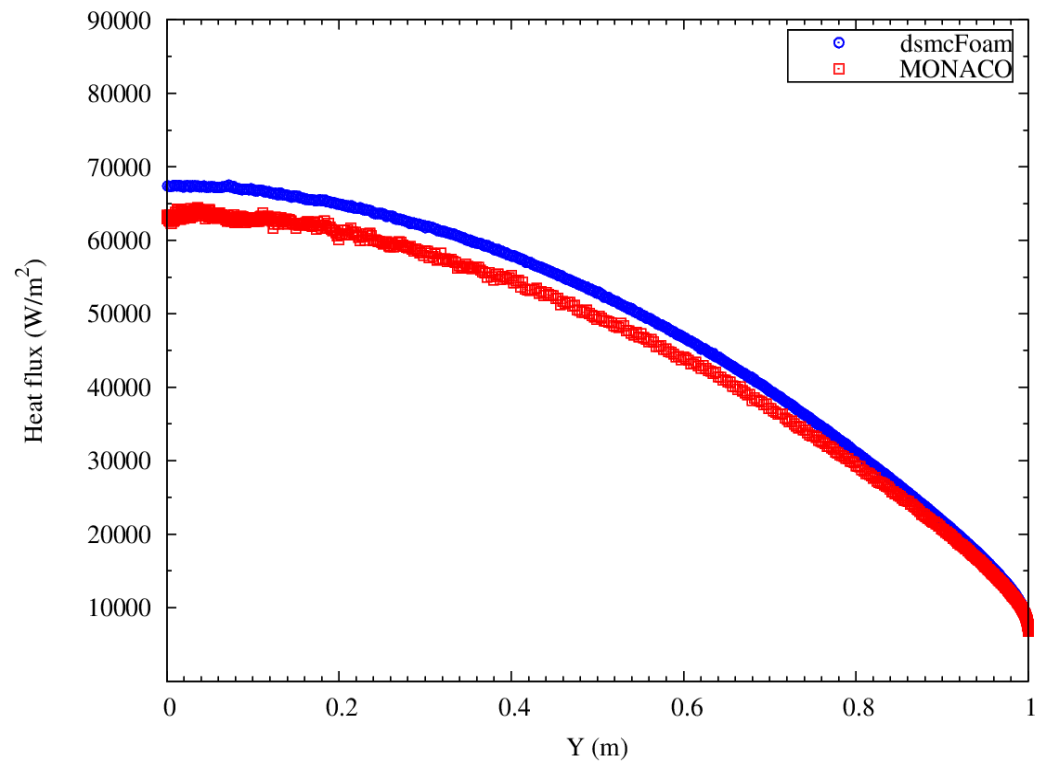




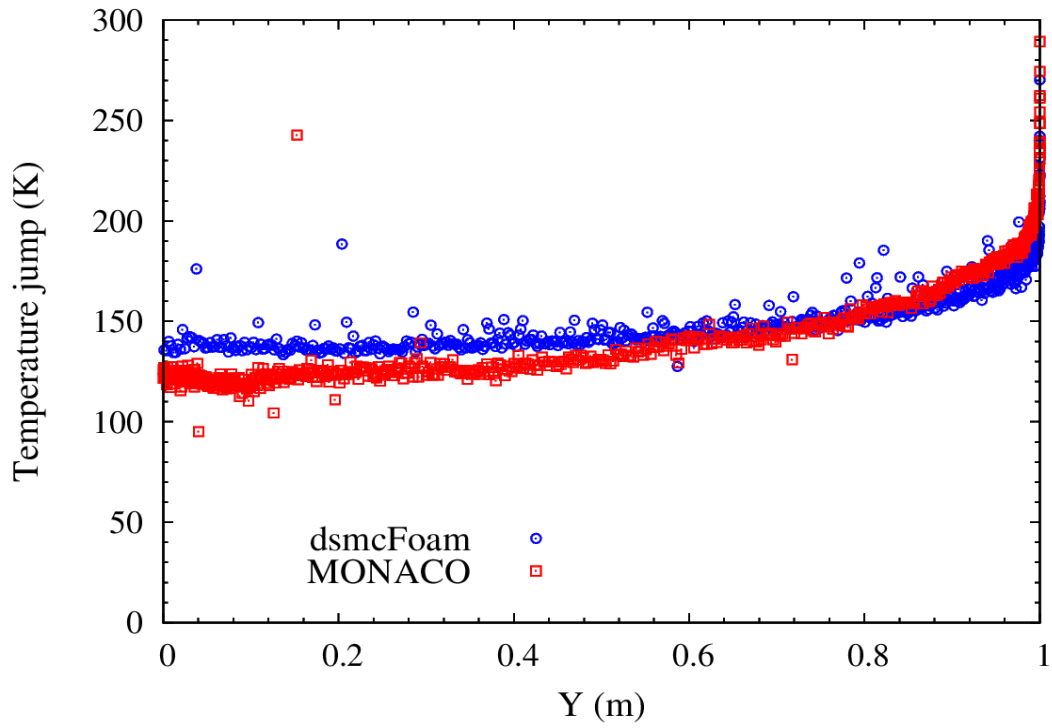
**Figure 16** Translational temperature contours predicted using dsmcFoam (Q-K) (lower half) and MONACO (TCE) (upper half) for reacting air flow over a 2D cylinder.



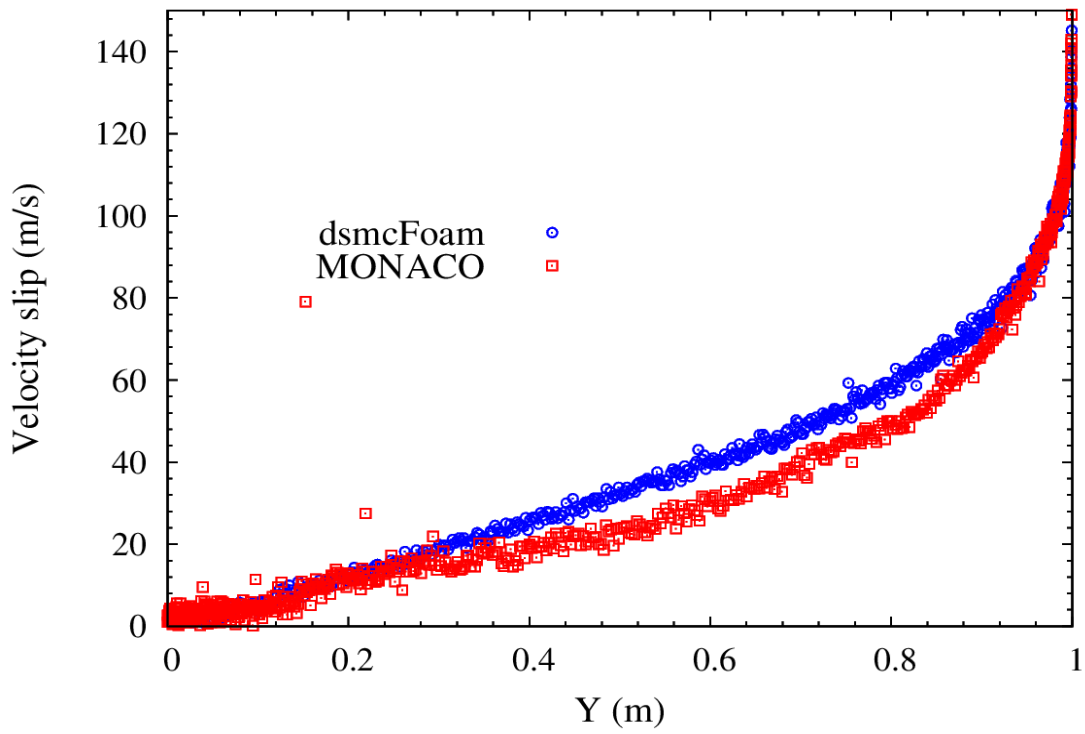
**Figure 17** *Cylinder surface pressure for reacting flow. Y is the vertical position above the stagnation point.*



**Figure 18** *Cylinder surface heat flux for reacting flow. Y is the vertical position above the stagnation point.*



**Figure 19** *Cylinder surface temperature-jump for reacting flow.  $Y$  is the vertical position above the stagnation point.*



**Figure 20** *Cylinder surface velocity-slip for reacting flow.  $Y$  is the vertical position above the stagnation point.*

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